



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/TR97/00018 <b>(22) International Filing Date:</b> 20 November 1997 (20.11.97) <b>(71) Applicant (for all designated States except US):</b> TÜBITAK-MARMARA RESEARCH CENTER [TR/TR]; PK.21, 41470 Gebze/Kocaeli (TR). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> BIROL, Yücel [TR/TR]; Tübitak-Marmara Research Center, PK.21, 41470 Gebze/Kocaeli (TR). <b>(74) Agent:</b> ANKARA PATENT BUREAU LTD.; Şehit Adem Yavuz Sokak 8/22, 06440 Kızılay Ankara (TR).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IN SITU PROCESS FOR PRODUCING AN ALUMINIUM ALLOY CONTAINING TITANIUM CARBIDE PARTICLES <b>(57) Abstract</b> <p>An in situ process is provided for producing an aluminium alloy containing titanium carbide particles, the process comprising introducing into an aluminium-titanium melt, graphite in bulk form, preferably manufactured in the form of a rotor, under conditions which facilitate the reaction of titanium in the melt with graphite to produce a dispersion of fine titanium carbide particles within the melt, and finally solidifying the melt so as to retain the uniform distribution of the in situ formed titanium carbide particles in the product. Aluminium alloys containing titanium carbide particles produced according to the process of the present invention are good candidates for various wear-resistant, light-weight composite material applications. Another preferred use for alloys produced by the present invention is as master alloys for grain refining aluminium-based metals, particularly those which are known to exhibit the so-called "positioning effect".</p> <div data-bbox="706 1186 1274 1522" data-label="Diagram"> </div>		

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## DESCRIPTION

IN SITU PROCESS FOR PRODUCING AN ALUMINIUM ALLOY  
CONTAINING TITANIUM CARBIDE PARTICLES.

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The present invention relates to an in situ process for producing aluminium alloys containing a uniform dispersion of fine titanium carbide particles and to the resulting alloy.

Aluminium alloys containing refractory carbide particles, also referred to as particulate-reinforced aluminium composites, possess a spectrum of advantages with respect to their monolithic counterparts and have received a great deal of attention recently, owing to their competitive prices, easy implementation and characteristic isotropic behavior. Aluminium alloys reinforced with titanium carbide particles are a prominent example of these hybrid materials which combine the ductility, toughness, electrical and thermal conductivity of the aluminium matrix with the strength, stiffness, hardness and wear resistance of the refractory carbides, leading to a unique combination of properties which cannot be achieved in either of the individual components by alloying and/or thermomechanical processing alone. Titanium carbide-reinforced aluminium composites are attractive candidates for various applications, particularly in the automotive sector, as they offer, in addition to favorable mechanical properties, substantial weight savings. Pistons and connecting rods are examples of such automotive applications where titanium carbide reinforced aluminium alloys are receiving serious consideration with such benefits as reduced weight and improved wear resistance. P.Rohatgi, *JOM*, 43(991)10-15.

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What makes aluminium alloys containing titanium carbide particles technologically very important is not only the promise they hold as structural composite materials with superior mechanical and physical properties but also the potential they have as grain refiners for aluminium-based metals. Eversince it was claimed that the grain refinement obtained in aluminium alloys by the addition of titanium was due to its carbide which formed as a result of the reaction of titanium with traces of carbon which is almost always present in aluminium melts, titanium carbide has been assumed to be the nucleant in aluminium alloys inoculated with hypoperitectic titanium concentrations. A.Banerji and W.Reif, *Metall.Trans.*, 17A(1986)2127-2137. This "carbide theory" has been generally accepted

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and has prompted many attempts to synthesize master alloys with a fine dispersion of titanium carbide particles in an aluminium matrix.

A variety of processing techniques have been employed to produce aluminium alloys containing titanium carbide particles. Powder Metallurgy methods were used to introduce titanium carbide particles into sintered aluminium in order to improve the mechanical properties and a notable improvement in wear resistance has been reported. G.W.Halldin et.al., *Progress in Powder Metallurgy*, 38(1983)593-611. Another process, which involves heating the powders of the elemental components of a high temperature ceramic phase in the presence of a third metallic phase constituting the matrix of the eventual product, produces a dispersion of fine ceramic particles in a compatible matrix by an exothermic reaction. A.R.C.Westwood, *Metall.Trans.*, 19A(1988)749-758. A variety of ceramic particles including carbides, borides and nitrides have been produced with this technique in a number of matrix materials including aluminium. Another process for producing composite materials, disclosed in U.S. Pat. No. 4,402,744, relies on sintering a mixture of carbon particles, aluminium powder and the powder of an aluminium-transition metal intermetallic compound, the transition metal being a refractory carbide-former such as titanium. The intermetallic phase is reduced by carbon to aluminium and a carbide such as titanium carbide to yield aluminium-based composites which are reinforced by carbon particles in addition to refractory carbide particles. While the attributes of the Powder Metallurgy route have long been recognized, it is more expensive, more sophisticated and pose serious health and safety hazards as it involves handling of fine metal/ceramic powders.

Solidification processing of aluminium alloys containing ceramic particles, on the other hand, is particularly attractive as it is economical and practical. It is carried out in practice generally by direct introduction of the particles into aluminium melts, by mechanical means. A variety of techniques have been proposed to introduce ceramic particles into metal melts. P.K.Rohatgi et.al., *Int.Met.Rev.*, 31(1986)115-139. This, however, is not a simple task as the ceramic particles are hardly wet by aluminium melts. Hence, either the ceramic particles or the aluminium melts ought to be treated by thermal, chemical and/or mechanical means to promote wetting. These pre-treatments increase the number of manufacturing steps involved and, thus, the cost of processing. A simpler method, comprising adding the non-wetted particles to a vigorously agitated, partially solidified

slurry of the alloy, was proposed to overcome this difficulty. A.Sato and R.Mehrabian, *Metall.Trans.*, 7B(1976)443-451. This compocasting technique was employed to reinforce an aluminium alloy with titanium carbide particles, with an average size of 30 microns, upto a volume fraction of %15. However, since the titanium carbide particles  
5 mechanically mixed into the molten aluminium are not in thermodynamic equilibrium, there is a potential risk of interface reactions which yield undesirable products at processing temperatures,  $Al_4C_3$  in particular, and lead to a substantial degradation in properties.

10 Many of the problems encountered in solidification processing of particulate-reinforced aluminium composites are overcome by an alternative approach which relies upon the in situ formation of titanium carbide particles in aluminium melts. Since titanium carbide particles so generated are thermodynamically stable, the matrix-particle interfaces tend to be clean, free from adsorbed gases, oxide films and detrimental reaction products and are  
15 thus much stronger.

One such approach involves the formation of titanium carbide particles in aluminium melts by a gas-molten metal reaction. In one embodiment of the process disclosed in U.S.Patent.No. 4,808,372, a carbon-bearing gas is introduced into a molten composition  
20 comprising aluminium as the matrix metal and a transition metal as the refractory carbide-forming component, allowing the transition metal in the melt to react with the carbon released from the injected gas to form a dispersion of carbide particles. In another embodiment of this invention, carbon is introduced into the melt in the form of a carbonaceous solid suspended in the gas. The composite materials of this patent,  
25 however, reveal several phases other than titanium carbide, the reinforcing phase of choice in the product when the matrix liquid is molten aluminium and the refractory carbide-forming component is titanium, including unreacted carbon and titanium and thus suffer from a low recovery of the carbon source as well as the carbide forming-transition metal. The unreacted titanium crystallizes in the form of titanium aluminide needles which impair  
30 the mechanical properties of the product. Ternary Al-Ti-C carbides which form in these materials have yet another adverse effect on the recovery situation in regard to the population of titanium carbide particles. Furthermore, gas injection of the carbonaceous component in the process of this invention introduces into the melt a quantity of gas which

is extremely difficult to remove since the viscosity of the melt increases with increasing volume fraction of particles.

Another in situ process to produce titanium carbide particles in aluminium alloys has  
5 been the subject of U.K. Pat. No. 8505904. The process disclosed in this patent essentially consists of thoroughly dispersing graphite particles of average size of about 20 microns into an Al-Ti melt, and causing the dispersed graphite particles to react with titanium within the melt so as to produce a dispersion of titanium carbide particles. This is accomplished by stirring the melt vigorously to generate one or more vortices into which  
10 carbon powder is added over an extended period of time. A preferred use for alloys produced by this invention is envisaged to be as grain refiners for aluminium-based metals. However, the process of this patent also fails to achieve complete conversion of titanium to titanium carbide. So, the product reveals excess titanium in the form titanium aluminide needles in addition to a number of phases, namely aluminium carbide and  
15 ternary Al-Ti-C phases, which have a deleterious effect on its grain refining capacity. Moreover, the vortices generated in the melt during the process of this invention leads to gas entrapment with an adverse effect on the quality of the product.

Among the several binary and ternary phases ( $\text{Al}_3\text{Ti}$ ,  $\text{Al}_4\text{C}_3$ ,  $\text{Ti}_2\text{AlC}$ ,  $\text{Ti}_3\text{AlC}$ ) which  
20 have been reported to form in aluminium-rich Al-Ti-C ternary alloys in addition to the alpha-aluminium solid solution, titanium carbide is the only phase which, being a refractory carbide, can be utilized as a reinforcing component in aluminium alloys. It is also fair to conclude from the so-called "carbide theory" that titanium carbide is the only (or the most effective) phase in the ternary Al-Ti-C system which is capable of refining the  
25 grain structure of aluminium-based metals. So, one would like to achieve, in a process to manufacture aluminium alloys with a dispersion of titanium carbide particles, whether they are destined to be used in structural applications to offer superior mechanical properties or as grain-refining master alloys, complete conversion of the titanium in the melt to the titanium carbide phase.

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The present invention provides an in situ process for producing aluminium alloys containing a dispersion of fine titanium carbide particles with improved homogeneity. In spite of the lack of success of prior attempts over many years, it is possible with the present invention to achieve full recovery of titanium as the refractory carbide-forming

component and to produce a good concentration of titanium carbide particles in the matrix. The method comprises introducing into an aluminium-titanium melt, graphite in bulk form, manufactured preferably in the form of a rotor, under favorable conditions which cause titanium in the melt to react with graphite spontaneously to form a dispersion  
5 of titanium carbide particles until the melt is depleted of titanium. Unlike prior art processes which require that a carbonaceous gas and/or the powder of a carbonaceous solid be used to introduce carbon into Al-Ti melts, the process of the present invention utilizes graphite in bulk form as the source of carbon, which is withdrawn from the melt once titanium is entirely carburized, thus avoiding any excess quantities of carbon  
10 entrapped in the cast alloy and also eliminating any risk of the supplied carbon being expelled out of the melt during the process. That this process does not require a precise balancing of the supply of carbon with respect to the titanium concentration in the melt is a further advantage offered by the present invention. The aluminium melt with a dispersion of in situ formed titanium carbide particles is finally solidified so as to retain the  
15 uniform distribution of carbide particles in the cast alloy.

The aluminium melt containing titanium for reaction with graphite to form titanium carbide particles once the graphite is introduced into the melt may be prepared by one of several ways known in the art, for example by melting a pre-existing Al-Ti master alloy,  
20 by melting an aluminium-based solid and a titanium-based solid together and mixing the two in the liquid state or by melting an aluminium-based solid and introducing into this melt a suitable titanium salt.

As it is possible to achieve complete conversion of titanium in the melt to titanium  
25 carbide with the present invention, the titanium concentration in the melt may be selected according to the level of reinforcement, i.e. the volume fraction of titanium carbide particles, desired in the final alloy. It is preferable to use a titanium concentration of more than 5 weight % in the melt in order to generate a population of titanium carbide particles which has a notable effect on the mechanical properties of the final alloy when destined to  
30 be used in structural applications and which offers sufficient grain refining-effect when destined to be used as a grain refiner for aluminium-based metals.

Experience has shown that increasing the titanium concentration in the melt has a favorable effect on the wetting of graphite by the Al-Ti melt which is essential for the

generation of titanium carbide particles in the melt. It should be kept in mind, however, that when a high concentration of titanium is used and is fully converted to titanium carbide, the fluidity of the melt is severely impaired and special measures may be necessary to successfully cast the melt.

5

We have found that it is very useful to superheat the Al-Ti melt to sufficiently high temperatures to allow for complete dissolution of the titanium aluminide intermetallic phase before introducing graphite into the melt. The temperature at which graphite is introduced into the melt can be readily estimated from the Al-Ti binary phase diagram and depends on the titanium concentration of the melt. Superheating the melt also helps to promote wetting of graphite by increasing its fluidity and by increasing the dissolved titanium concentration in the melt.

The source of carbon for the carburization of titanium in the melt in the process of the present invention is bulk graphite introduced into the melt in the form of a rotor. The rotor is designed with certain features to increase its surface area and thus its contact with the melt. It is fixed to a motor-driven shaft, preferably also made of graphite and is rotated inside the melt until the melt is depleted of dissolved titanium and is saturated with titanium carbide particles. The shaft may be manufactured out of clay/ceramic coated steel rod as well. Its size and dimensions depend on the size of the melt to be treated and the dimensions of the crucible used. The total weight of carbon introduced into the melt in this fashion is far greater than that required to carburize the titanium in the melt. The remaining graphite is withdrawn from the melt at the end of the process. The shaft has to be regarded as a consumable component as it is partially consumed during the process, very much like the rotor head, when manufactured out of graphite.

There are numerous ways well known in the art to supply heat to prepare an aluminium-titanium melt and to maintain this melt with a sufficient degree of superheat while treating it with a graphite rotor to generate titanium carbide particles in the melt. We prefer induction heating as it provides at the same time effective stirring action in the melt by electromagnetic means. Stirring is a very essential element of the process of the present invention as it facilitates continuous exposure of graphite to unreacted titanium and helps to detach and disperse the titanium carbide particles that form on the surface of the graphite rotor before they grow too large. Experience has shown that the results obtained



with the melt stirred sufficiently cannot be reproduced when it is at rest while being treated with graphite. When methods other than induction heating are employed to supply heat, it is important to stir the melt by mechanical means. We have found it very efficient to use the graphite rotor itself as a stirrer with minor revisions in its design, particularly  
5 when heat is supplied by means other than an induction coil such as an electrical resistance furnace but also when induction heating is employed in the process.

An inert vessel may be used in melting of the alloy and in holding of the melt during the process. A graphite crucible may also be used. The reaction of the melt with the crucible  
10 has to be accounted for when a graphite crucible is used. Experience has shown that the generation of titanium carbide particles is accelerated in the case of a graphite crucible with a favorable effect on the duration of the treatment. The duration of the treatment is affected by a number of other process variables as well: namely, the intensity of stirring, the titanium concentration of the original alloy, the temperature of treatment and the  
15 design and dimensions of the graphite rotor. It can be easily estimated for a given set of conditions with a trial run during which small melt samples are quenched in the course of the treatment. Metallographic evaluation of these samples provides very useful information as to when the process shall be terminated for the set of conditions which have prevailed during that particular run.

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We have found out that  $Al_4C_3$  starts to form when the melt is nearly saturated with titanium carbide particles, i.e. when it is nearly devoid of dissolved titanium. Since  $Al_4C_3$  is not desired in the final alloy as it is a brittle compound which decomposes readily when exposed to atmospheric moisture, it is best to leave some titanium unreacted to avoid the  
25 risk of getting  $Al_4C_3$  in the cast alloy. So, we prefer to terminate the process just before the melt is depleted of dissolved titanium.

Once the treatment of the melt with graphite is terminated the graphite rotor is withdrawn from the melt. The melt is skimmed and is stirred thoroughly before it is finally  
30 cast into the desired form. It is very beneficial to impose high cooling rates during solidification of the melt in order to suppress segregation of the particles and to retain a uniform distribution in the cast alloy. Typical microstructure of the alloys produced by processes practiced according to the present invention consists of a uniform dispersion of titanium carbide particles in the alpha-aluminium matrix. The in situ-formed titanium

carbide particles are very small, generally less than 3 microns in size and are very nicely wet by the matrix phase with no detrimental interaction zones at the interface.

In order that the present invention be better understood, it will now be described in more detail with reference to the following specific, non-limiting example with reference to the accompanying drawings, wherein:

FIG. 1 shows a sketch of the set-up used for producing aluminium alloys containing titanium carbide particles; and

FIG. 2 shows the optical micrograph, at a magnification of 40:1, of the resulting alloy produced in accordance with the present invention.

### EXAMPLE 1

Several small ingots of an aluminium-titanium master alloy, containing 95 percent by weight of aluminium and 5 percent by weight of titanium and weighting in total approximately 1 kilogram, were induction melted. An aluminium oxide crucible with a capacity of 1.8 kilograms of aluminium was used along with a graphite susceptor to achieve an efficient melting. The melt thus obtained was superheated to 1150 degrees Celsius at a rate of 10 degrees Celsius per minute before a graphite rotor was immersed into the melt. The rotor was manufactured out of a cylindrical graphite block, 70 millimeters in diameter and 35 millimeters in length, by machining four evenly spaced grooves along its entire length, each having a maximum depth of 15 millimeters. The rotor was fixed to a motor-driven shaft also made of graphite, having a diameter of 12 millimeters. The temperature of the melt was monitored by a chromel-alumel thermocouple and was maintained at about 1150 degrees Celsius throughout the process. The surface of the melt was covered with a salt flux. The rotor was rotated inside the melt at 100 revolutions per minute. The operation was terminated after 60 minutes and the melt was skimmed and thoroughly stirred with graphite rods. It was then poured into a permanent mold and squeezed into rectangular plates with a plunger.

The cast plates were subjected to microstructural examination by optical and scanning electron microscopy which revealed a homogeneous distribution of particles on every section taken from the rectangular plates. The particles were identified by x-ray and Energy Dispersive Spectroscopy (EDS) analysis as titanium carbide. The titanium carbide

particles were generally smaller than 3 microns and occasionally formed rather small clusters. Couple of very small titanium aluminide particles could also be detected only at higher magnifications. Only the reflections of the alpha aluminium solid solution and of the titanium carbide phases could be identified in the x-ray spectrum of these plates with  
5 no evidence of ternary carbides and the  $Al_4C_3$  phase.

## CLAIMS

We claim:

- 5 1) An in situ process for producing an aluminium alloy containing titanium carbide particles, the process comprising introducing into an aluminium-titanium melt, graphite in bulk form, under conditions which facilitate the reaction of titanium in the melt with graphite to produce a dispersion of fine titanium carbide particles within the melt, and finally solidifying the melt so as to retain the uniform distribution of the in situ formed  
10 titanium carbide particles in the product.
- 2) A process according to claim 1, wherein the graphite element introduced into the melt is provided in the form of a specially designed rotor.
- 3) A process according to claim 2, wherein the graphite rotor introduced into the melt is wet by the melt.
- 15 4) A process according to claim 2, wherein the graphite rotor is introduced into the melt under an inert atmosphere.
- 5) A process according to claim 2, wherein the graphite rotor is introduced into the melt under such conditions that the titanium in the melt is completely dissolved.
- 6) A process according to claim 2, wherein the melt is superheated to 1150 degrees  
20 Celsius before the graphite rotor is introduced into the melt.
- 7) A process according to claim 1, wherein the weight of graphite introduced into the melt is at least as much as that required to completely carburize the titanium in the melt.
- 8) A process according to claim 2, wherein the alloy produced comprises 2 to 20 weight% titanium and 0.5 to 5 weight% carbon, balance aluminium and incidental  
25 impurities.
- 9) A process according to claim 2, wherein at least 95 weight% of the titanium in the melt has reacted to form titanium carbide particles.
- 10) A process according to claim 2, wherein the melt is subjected to stirring by electromagnetic means.
- 30 11) A process according to claim 2, wherein the melt is stirred by mechanical means once the graphite rotor is introduced into the melt.
- 12) A process according to claim 2, wherein the graphite rotor serves as a stirrer as well as the source of carbon.

- 13) A process according to claim 2, wherein the graphite rotor introduced into the melt is rotated at 50-500 revolutions per minute.
- 14) A process according to claim 2, wherein the graphite block introduced into the melt is rotated at approximately 100 revolutions per minute.
- 5 15) A process according to claim 2, wherein the melt is provided and maintained during the treatment in a graphite crucible.
- 16) A process according to claim 2, wherein the size of the titanium carbide particles formed in situ fall in the range 0.5 to 10 microns.
- 17) An aluminium alloy containing titanium carbide particles produced by the process  
10 of claim 1.
- 18) An aluminium alloy containing titanium carbide particles produced by the process of claim 2.
- 19) An aluminium alloy containing titanium carbide particles produced by the process of claim 3.
- 15 20) An aluminium alloy containing titanium carbide particles produced by the process of claim 4.
- 21) An aluminium alloy containing titanium carbide particles produced by the process of claim 5.
- 22) An aluminium alloy containing titanium carbide particles produced by the process  
20 of claim 6.
- 23) An aluminium alloy containing titanium carbide particles produced by the process of claim 7.
- 24) An aluminium alloy containing titanium carbide particles produced by the process of claim 8.
- 25 25) An aluminium alloy containing titanium carbide particles produced by the process of claim 9.
- 26) An aluminium alloy containing titanium carbide particles produced by the process of claim 10.
- 27) An aluminium alloy containing titanium carbide particles produced by the process  
30 of claim 11.
- 28) An aluminium alloy containing titanium carbide particles produced by the process of claim 12.
- 29) An aluminium alloy containing titanium carbide particles produced by the process of claim 13.

30) An aluminium alloy containing titanium carbide particles produced by the process of claim 14.

31) An aluminium alloy containing titanium carbide particles produced by the process of claim 15.

5 32) An aluminium alloy containing titanium carbide particles produced by the process of claim 16.

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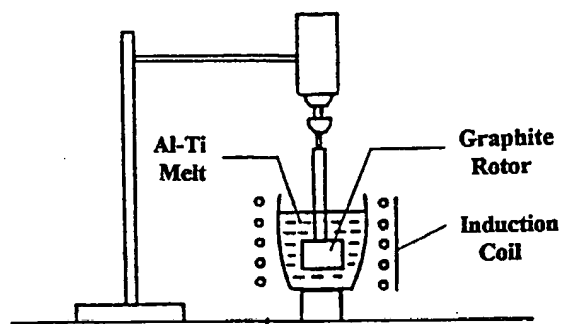


FIGURE 1



FIGURE 2

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR 97/00018

## A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>6</sup>: C 22 C 1/10, 21/00

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 244 949 A 1 (INCO ALLOYS INTERNATIONAL INC.) 11 November 1987 (11.11.87), claims 1-7.	1-32
A	WO 86/05 212 A1 (LONDON & SCANDINAVIAN METALLURGICAL CO) 12 September 1986 (12.09.86), abstract.	1-32
A	Database WPI on Questel, week 9202, London:Derwent Publications Ltd., AN 92-049531, CA 2017144 A (CARON S.), abstract.	1-32
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# INTERNATIONAL SEARCH REPORT

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EP A1	244949	11-11-87	AT E AU A1 AU B2 BR A DE C0 EP B1 ES T3 JP A2 JP B4 US A	69065 709387 588990 8701509 3774169 244949 2025651 62238344 5083624 4624705
WO A1	8605212	12-09-86	GB A0 GB A1 AT E AU A1 AU B2 BR A CA A1 DE C0 EP A1 EP B1 JP T2 JP B4 NO A NO B NO C US A US A GB A0	8519447 2171723 63574 55112786 595187 8605619 1289748 3679263 214220 214220 62502201 8016234 864195 167589 167589 4748001 4842821 8505904